Chemical, Biological & Environmental Engineering

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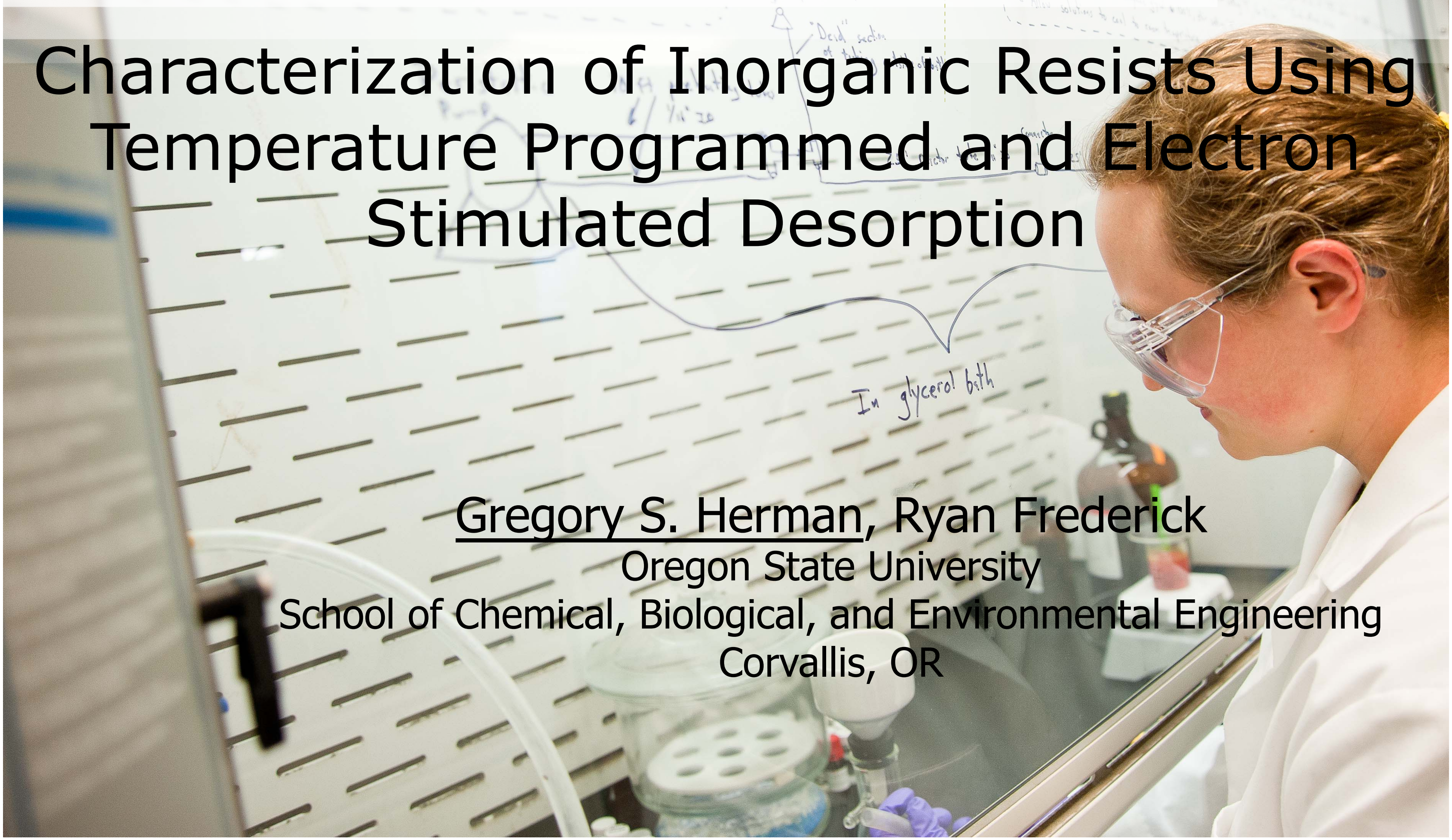
COLLEGE OF ENGINEERING

Characterization of Inorganic Resists Using Temperature Programmed and Electron Stimulated Desorption



Gregory S. Herman, Ryan Frederick

Oregon State University

School of Chemical, Biological, and Environmental Engineering

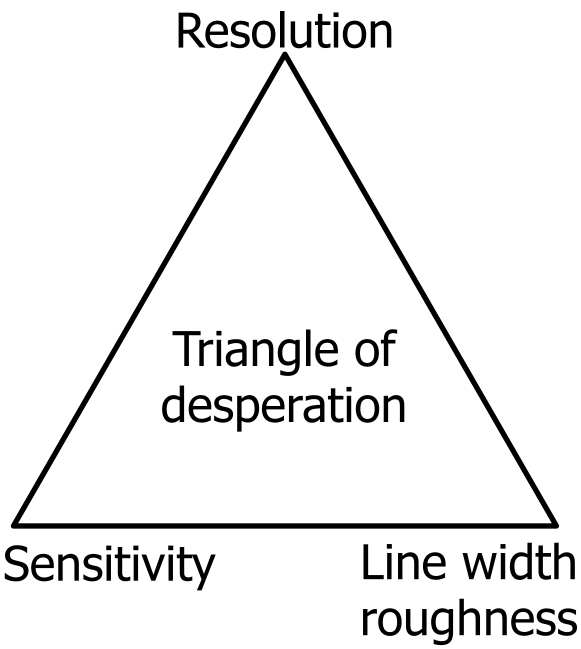
Corvallis, OR

Critical Challenges for EUV Photoresists

Challenge	Areas to focus
EUV interaction with resist	High EUV quantum yield, low electron affinity, reduce electron blur
Resolution	Improve contrast, swelling control, reduce diffusion, electron scattering, minimize acid diffusion
Line width roughness	Improve resist homogeneity, aggregation mitigation, minimize acid diffusion
Photospeed	EUV sensitization (higher cross sections)
Pattern Collapse	Reduced aspect ratios (thinner films)
Defects	Aggregation mitigation, improve resist homogeneity
High selectivity to etch process	Integration of inorganic functionality

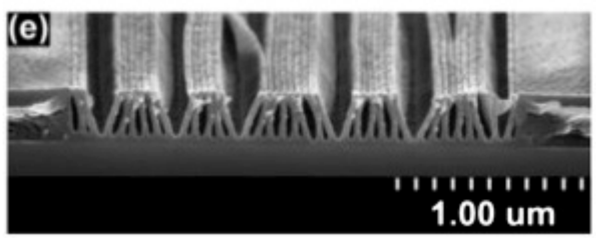
J.W. Thackeray, Proc. of SPIE Vol. 7972, 797204

Lithographic Uncertainty Principle



	Resolution (pitch in nm)	Sensitivity ($\mu C/cm^2$)	Line width roughness (nm)
PMMA[1] (organic)	20	6000	2-3 nm
HSQ[2] (inorganic)	9	10000	< 2 nm
HafSOx[3] (inorganic)	21	800	< 2 nm

[1]H. Duan *et al., JVST B* **28**, C6C58 (2010)
[2]J. K. W. Yang *et al., JVST B* **27**, 2622 (2009)
[3]A. Telecky *et al., JVST B* **28**, C6S19 (2010)



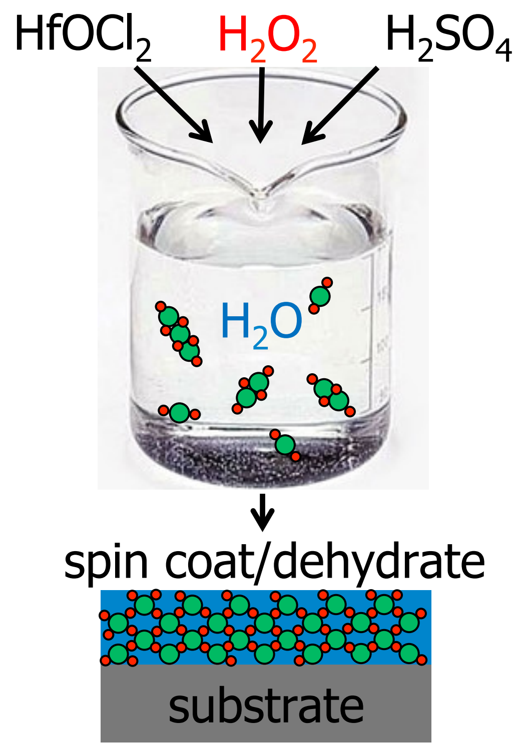
Pattern collapse on a 70 nm pitch with dose of 1.65 nC/cm^2

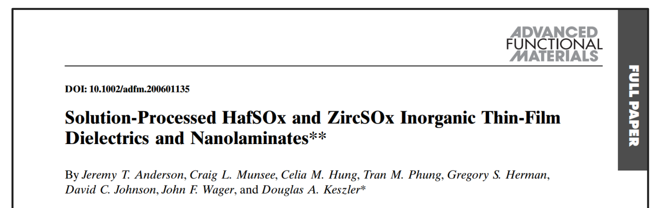
M. A. Mohammad, et al. Nanoscale Res. Lett. 8, 139 (2013)

Background

Solution-based nanolaminates

- Sub-10 nm layer thicknesses.
- Smooth surfaces enabled by inorganic nanoclusters formed in solution.
- Can nanopatterning be extended to lateral dimensions?



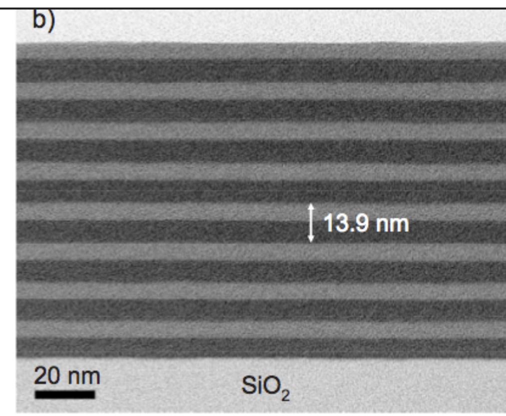

ADVANCED FUNCTIONAL MATERIALS

FULL PAPER

DOI: 10.1002/adfm.200601135

Solution-Processed HafSOx and ZircSOx Inorganic Thin-Film Dielectrics and Nanolaminates**

By *Jeremy T. Anderson, Craig L. Munsee, Celia M. Hung, Tran M. Phung, Gregory S. Herman, David C. Johnson, John F. Wager*, and *Douglas A. Keszler**



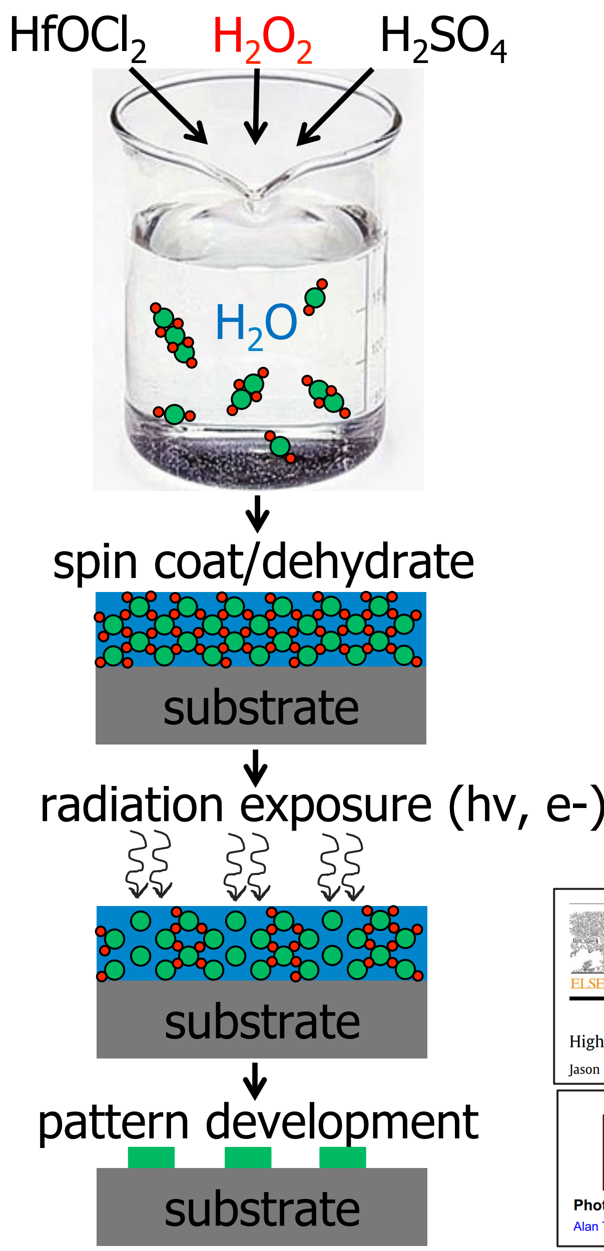
Background

Lateral nanopatterning

- Requires complexation of radiation sensitive component that controls solubility.

- HafSOx and ZircSOx nanoclusters with hydrogen peroxide shown to be promising.

- Results in negative tone resist (resist remains in locations exposed to radiation).



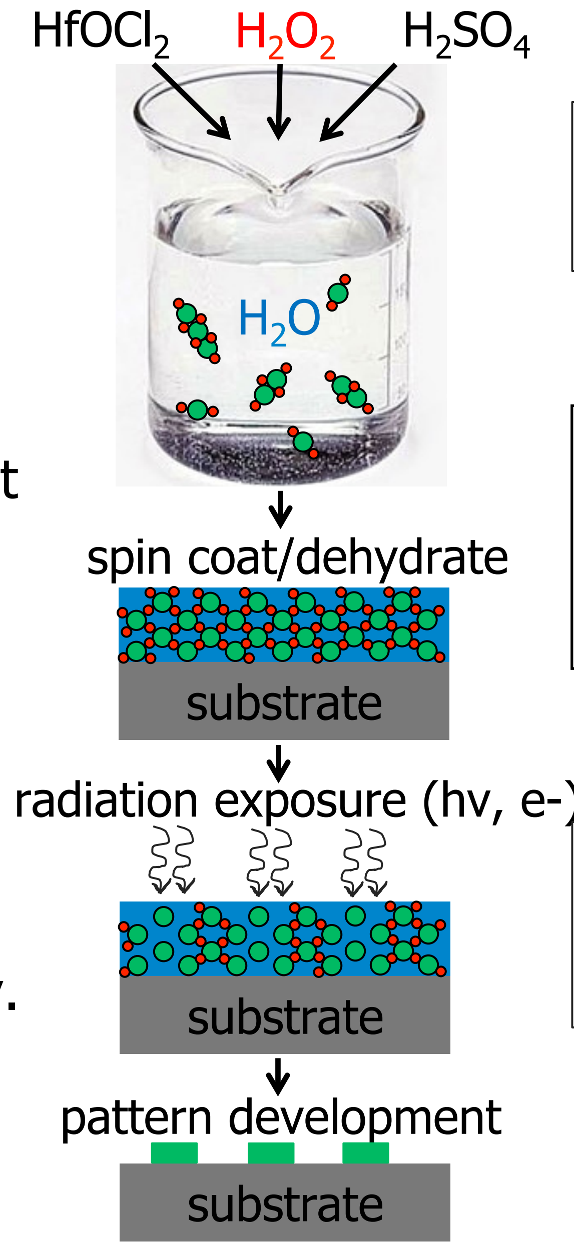

Contents lists available at ScienceDirect
Microelectronic Engineering
journal homepage: www.elsevier.com/locate/mee
ELSEVIER
High resolution, high sensitivity inorganic resists
Jason Stowers *, Douglas A. Keszler


JVSTB
Journal of Vacuum Science & Technology B
Photopatternable inorganic hardmask
Alan Telecky, Peng Xie, Jason Stowers, Andrew Grenville, Bruce Smith, and Douglas A. Keszler

Background

Lateral nanopatterning

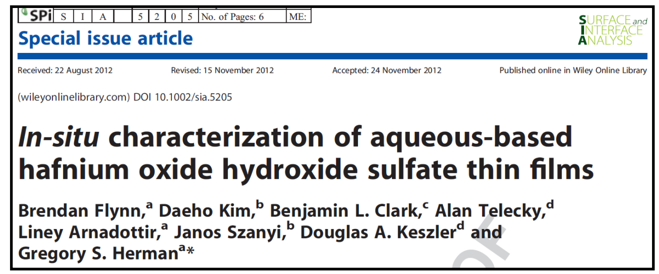
- Hafnium tetramers stabilized in solution by hydrogen peroxide.
- Thermal treatments result in significant dehydration of HafSOx and formation of
  Hf-O-Hf bonding.
- Sub 10 nm high density patterns can be obtained using e-beam lithography.




Inorganic Chemistry — Article — pubs.acs.org/IC

Hafnium Sulfate Prenucleation Clusters and the Hf_{18} Polyoxometalate Red Herring

Rose E. Ruther,[†,‡] Brenna M. Baker,[†,‡] Jung-Ho Son,[†,§] William H. Casey,[†,§] and May Nyman[*,†,‡]


SURFACE and INTERFACE ANALYSIS

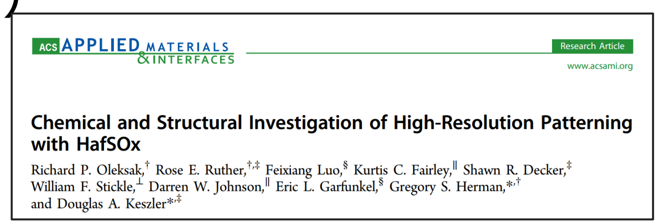
Special issue article

Received: 22 August 2012 Revised: 15 November 2012 Accepted: 24 November 2012 Published online in Wiley Online Library

(wileyonlinelibrary.com) DOI 10.1002/sia.5205

***In-situ* characterization of aqueous-based hafnium oxide hydroxide sulfate thin films**

Brendan Flynn,[a] Daeho Kim,[b] Benjamin L. Clark,[c] Alan Telecky,[d] Liney Arnadottir,[a] Janos Szanyi,[b] Douglas A. Keszler[d] and Gregory S. Herman[a*]


ACS APPLIED MATERIALS & INTERFACES — Research Article — www.acsami.org

Chemical and Structural Investigation of High-Resolution Patterning with HafSOx

Richard P. Oleksak,[†] Rose E. Ruther,[†,‡] Feixiang Luo,[§] Kurtis C. Fairley,[∥] Shawn R. Decker,[‡] William F. Stickle,[⊥] Darren W. Johnson,[∥] Eric L. Garfunkel,[§] Gregory S. Herman,[*,†] and Douglas A. Keszler[*,‡]

Background

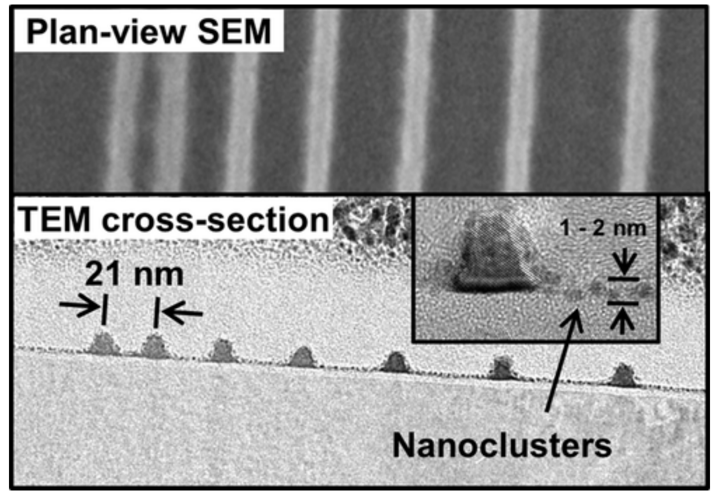
HafSOx - nanopatterning

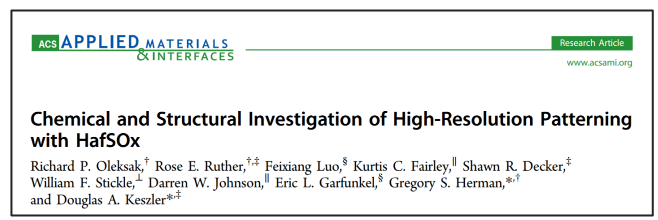
spacer group

thermal chemistry

$$Hf(SO_4)_{0.7}(O_2)_{0.5}(OH)_{1.6}\cdot xH_2O$$

radiation induced chemistry




ACS APPLIED MATERIALS & INTERFACES
Research Article
www.acsami.org

Chemical and Structural Investigation of High-Resolution Patterning with HafSOx

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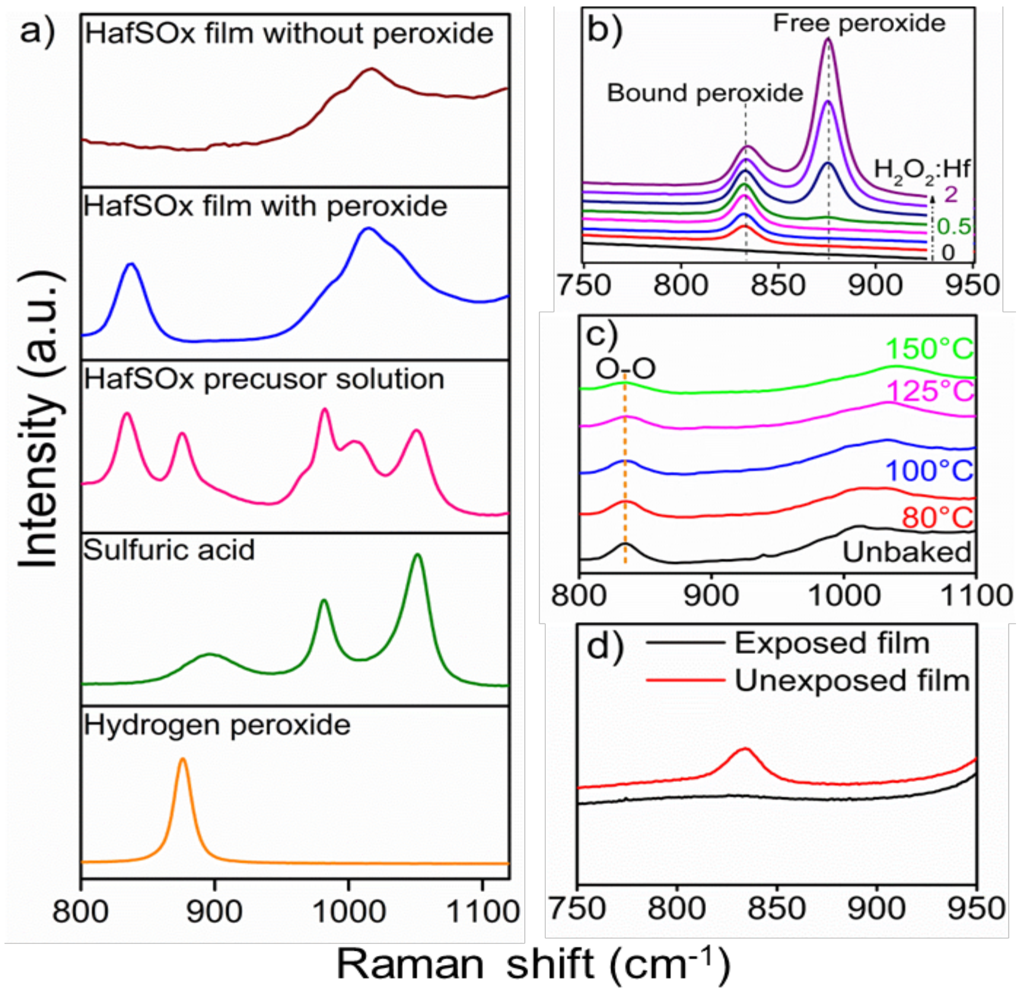
Raman Characterization of HafSOx

Peroxide and sulfate bind to Hf-clusters in solution.

Films retain primarily bound peroxide and sulfate.



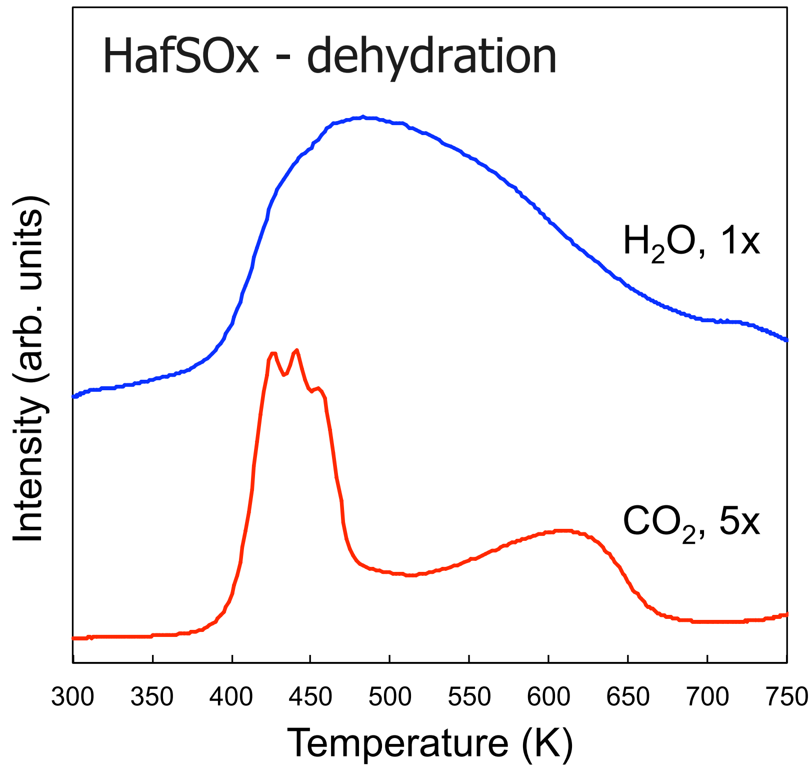
Bound peroxide saturates at 0.5 O_2 per Hf.

Bound peroxide is thermally stable, but readily decomposes on radiation exposure.

R. E. Ruther, F. Luo , R. P. Oleksak, J. M. Amador, S. R. Decker, M. N. Jackson, J. R. Motley, D. W. Johnson, G. S. Herman, E. L. Garfunkel, D. A. Keszler, in preparation.

Temperature Programmed Desorption

Thermal chemistry



thermal chemistry

$$Hf(SO_4)_{0.7}(O_2)_{0.5}(OH)_{1.6} \cdot xH_2O$$

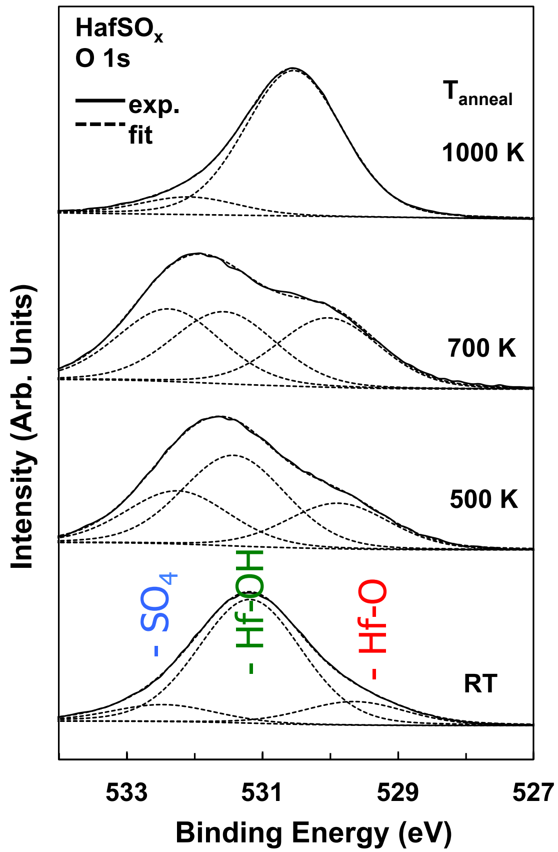
radiation induced chemistry

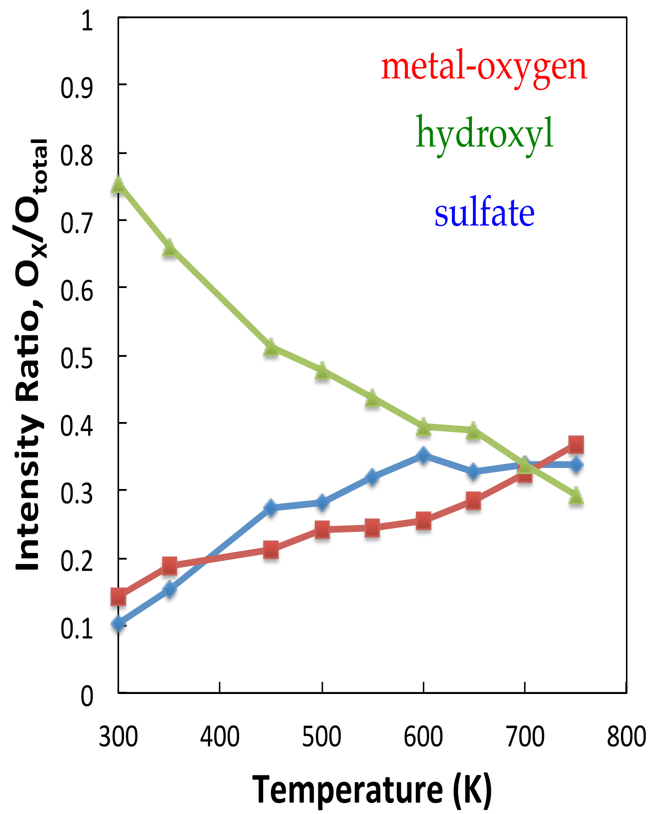
$$Hf(OH)_2Hf(OH)_2 \xrightarrow{\Delta} >HfO_2Hf< + H_2O$$

B. Flynn, et al., Surf. Interface Anal. 46, 210 (2014)

X-ray Photoelectron Spectroscopy

Thermal chemistry

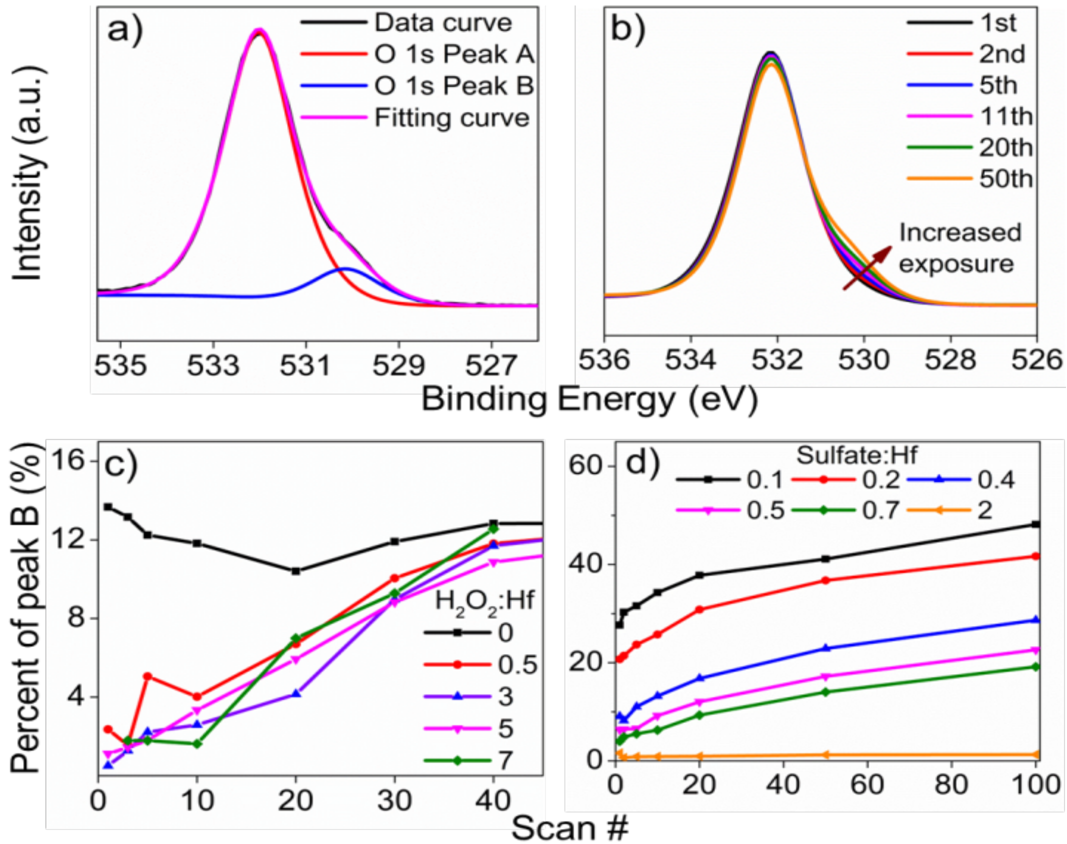




B. Flynn, et al., Surf. Interface Anal. 46, 210 (2014)

X-ray Induced Chemistries in HafSOx

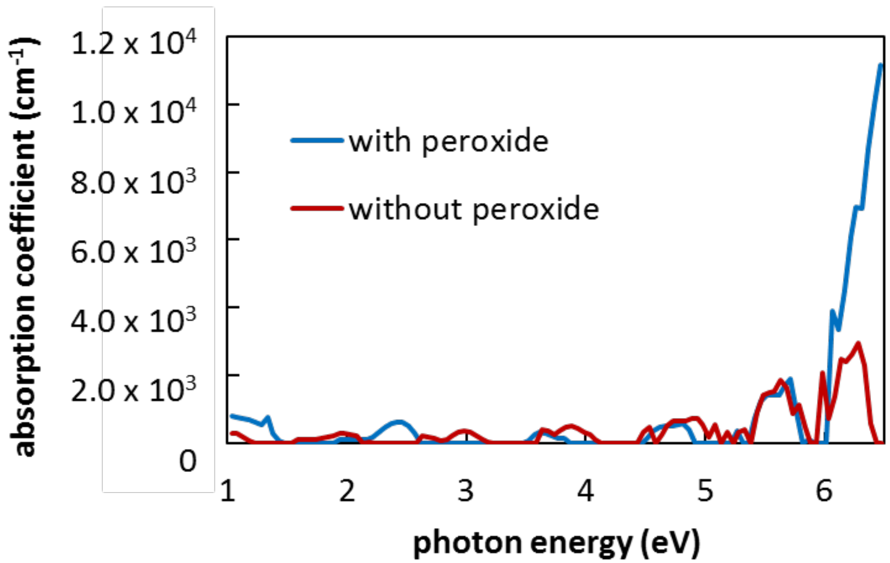
hv = 1487 eV

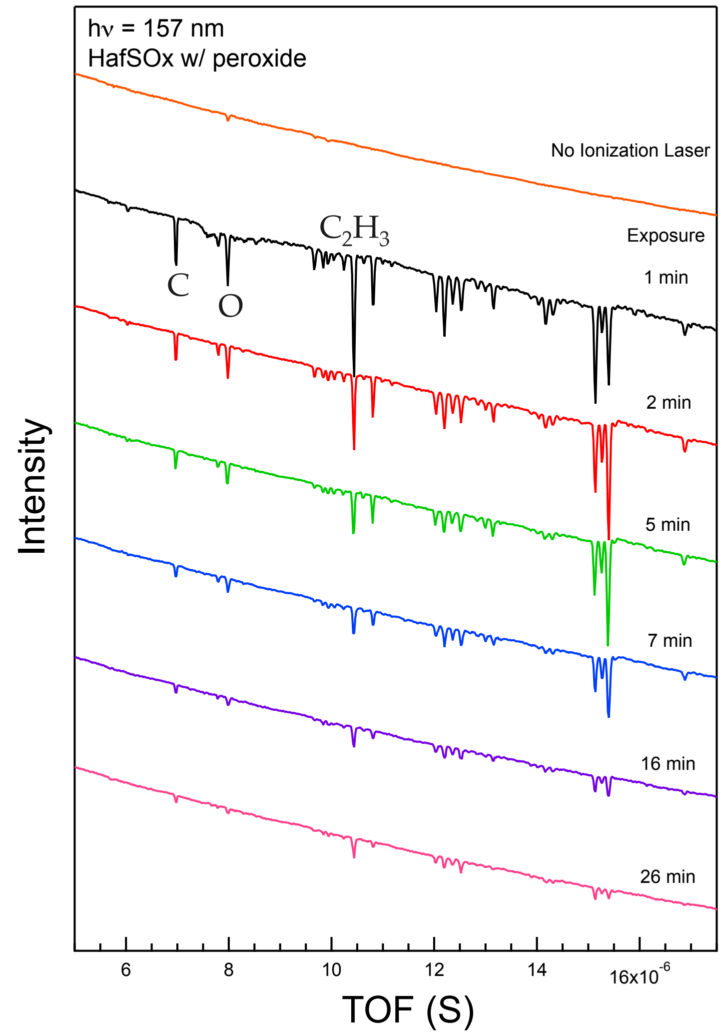


R. E. Ruther, F. Luo , R. P. Oleksak, J. M. Amador, S. R. Decker, M. N. Jackson, J. R. Motley, D. W. Johnson, G. S. Herman, E. L. Garfunkel, D. A. Keszler, in preparation.

Photon Induced Chemistries in HafSOx

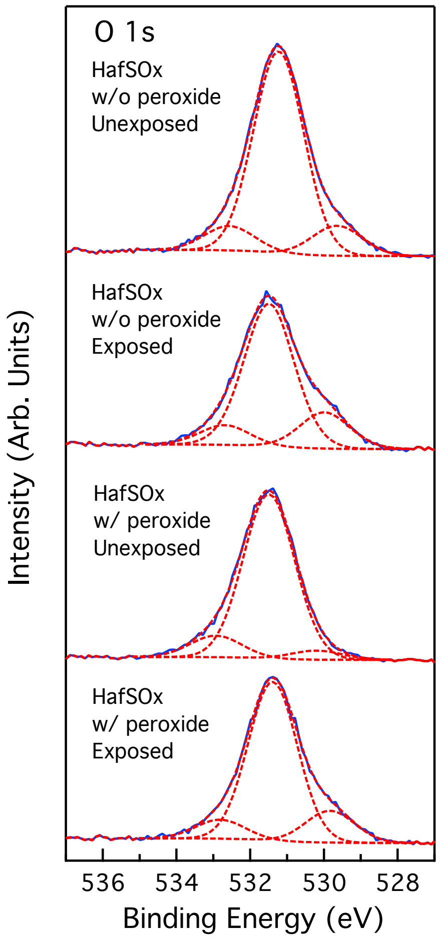
Photon stimulated desorption
hv = 157 nm (7.9 eV)
Laser power ~30 mJ/s





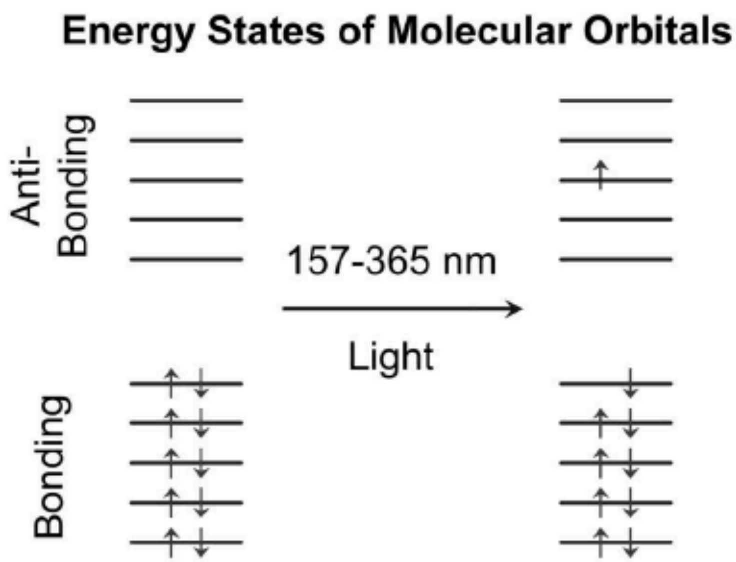
Photon Induced Chemistries in HafSOx

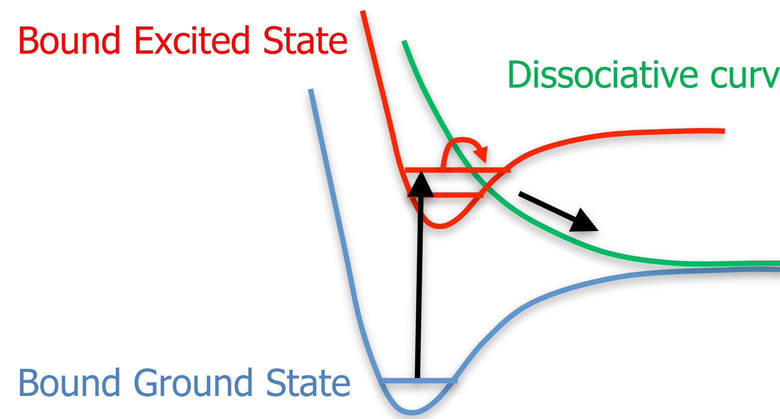
Photon induced chemistry
hv = 157 nm (7.9 eV)

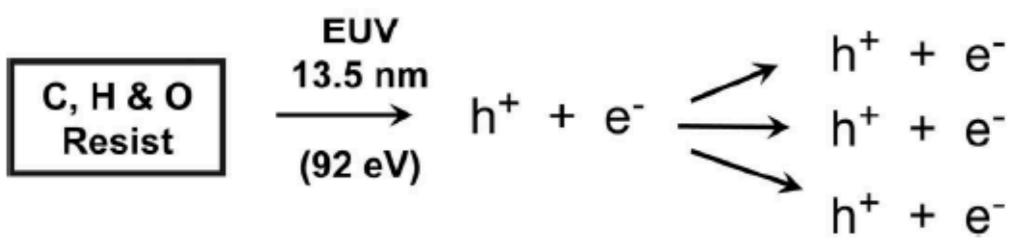


Sample	B.E. (eV)			% Area		
	High B.E. peak	Middle B.E. peak	Low B.E. peak	High B.E. peak (SO_4)	Middle B.E. peak (Hf-OH)	Low B.E. peak (Hf-O-Hf)
HafSOx w/o peroxide Unexposed	532.6	531.2	529.6	8.2	81.1	10.7
HafSOx w/o peroxide Exposed	532.8	531.5	530.0	8.1	73.2	18.7
HafSOx w/ peroxide Unexposed	533.1	531.7	530.7	9.5	82.9	7.6
HafSOx w/ peroxide Exposed	533.0	531.4	529.9	5.9	80.0	14.2

Resist Exposure Mechanisms







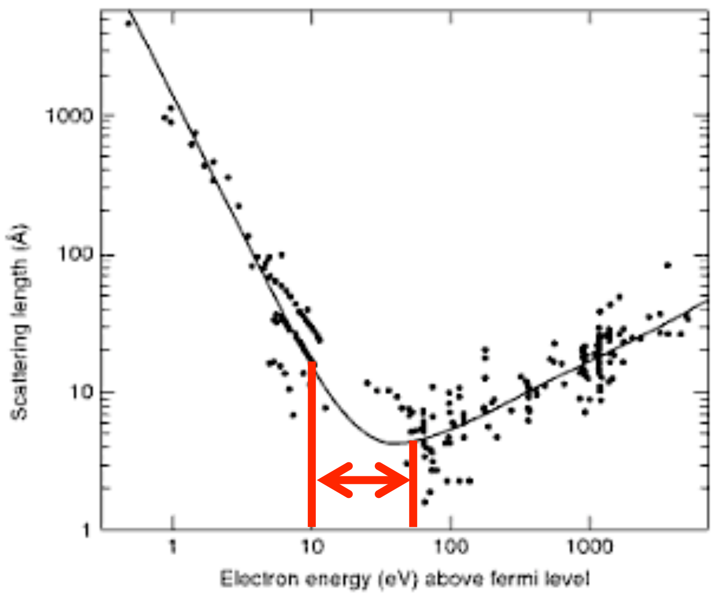
EUV Lithography, SPIE, editor V. Bakshi, Chap. 8, R. L. Brainard

Role of Electrons in Nanopatterning

Low energy electrons (< 90eV) from EUV radiation, not EUV photons, may be primary species driving radiation induced chemistries

Characterize low energy electron interaction with HafSOx

Basics on electron scattering in solids:



M. P. Seah and W. A. Dench, Surf. Interface Anal. 1, 2 (1979)

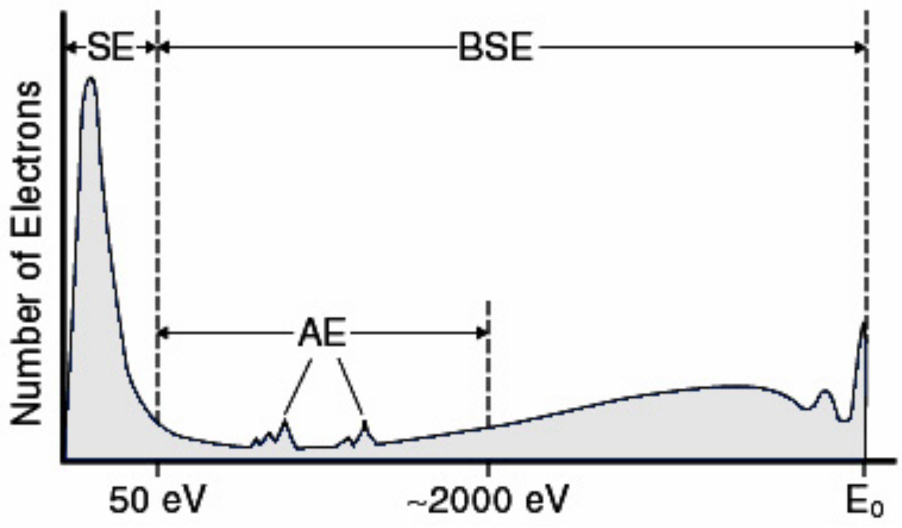
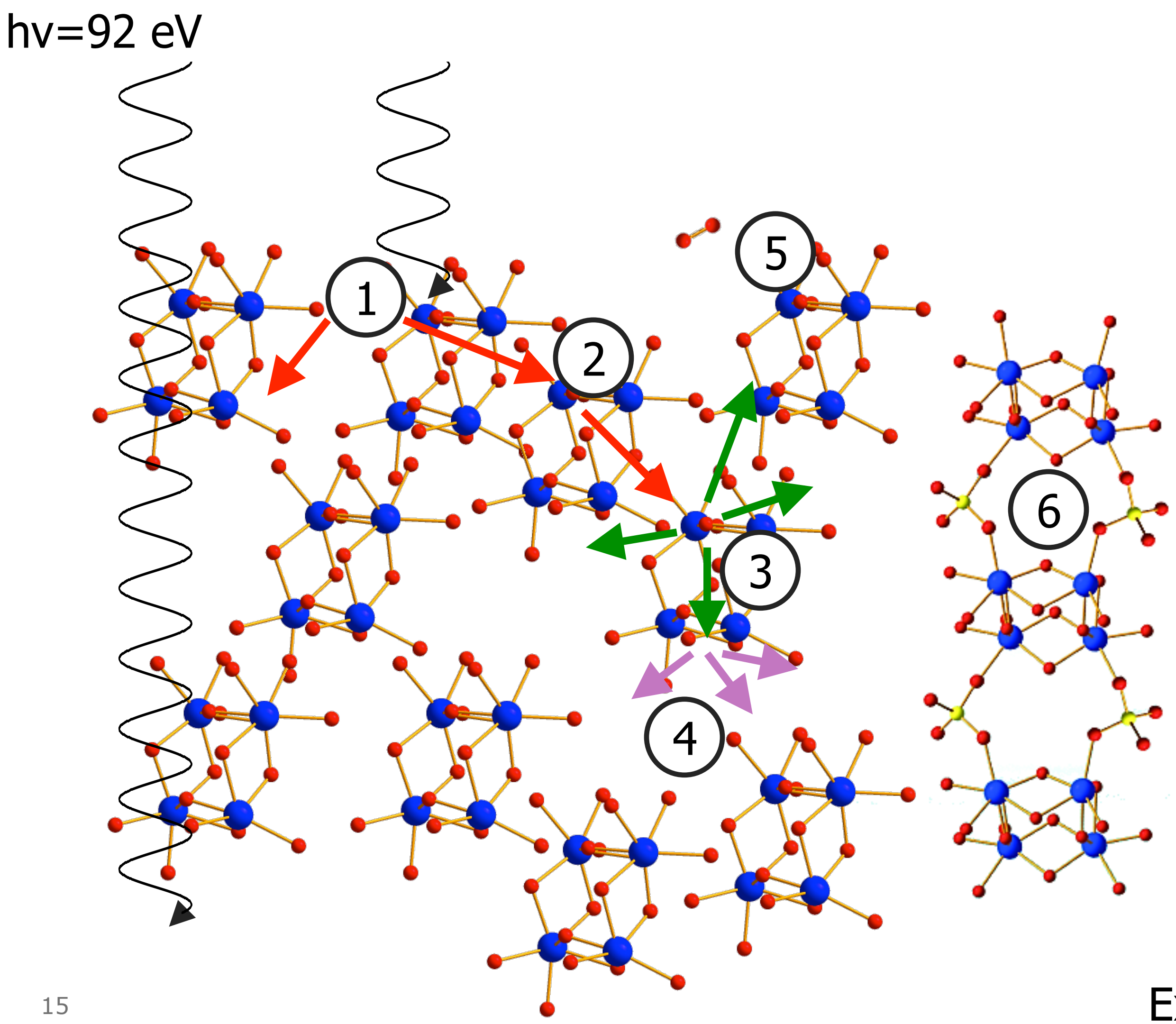


Figure after Goldstein et al. 1981.

Interaction of HafSOx with EUV



Anisotropic

1. Photon absorption (high Hf absorption cross section)
2. Electron scattering

Isotropic

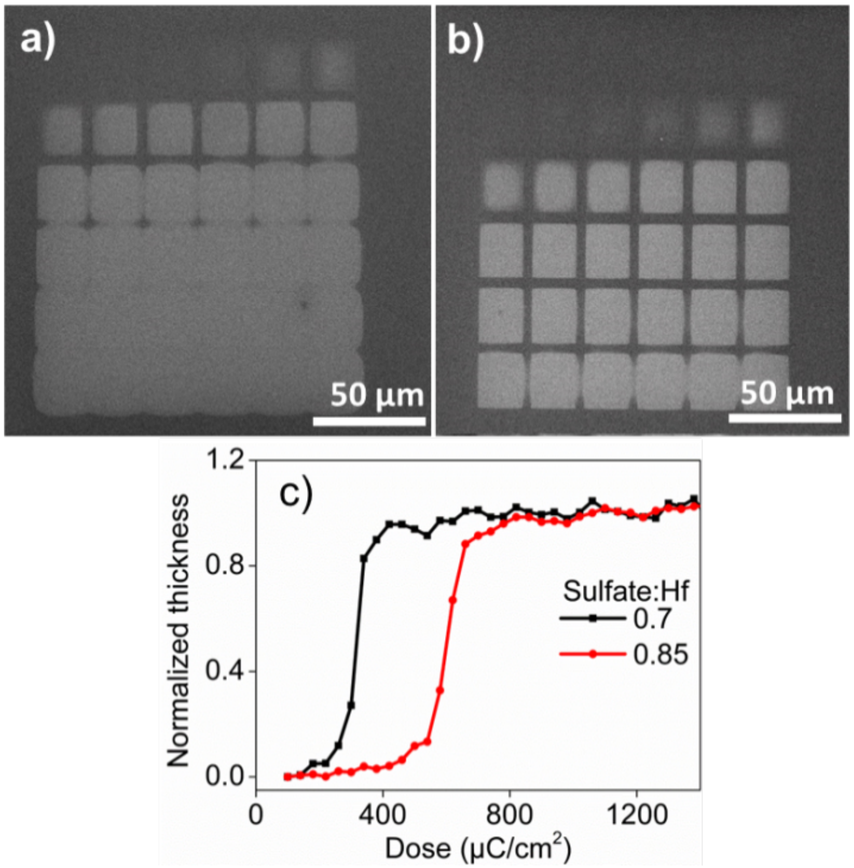
3. Secondary electrons (E_{kin} ~ 20-80 eV)
4. Thermal electrons (E_{kin} < 15 eV)
5. O_2 desorption
6. Condensation reactions

Expected yield > 4 e^-/photon

HafSOx as an eBeam Resist

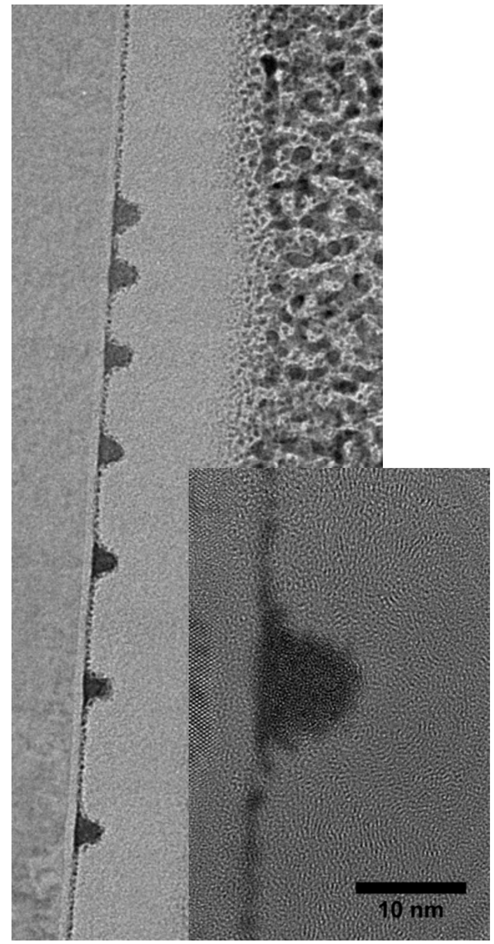
Electron induced chemistry

100 to 1500 μC/cm^2 in increments of 40 μC



R. E. Ruther, et al., in preparation

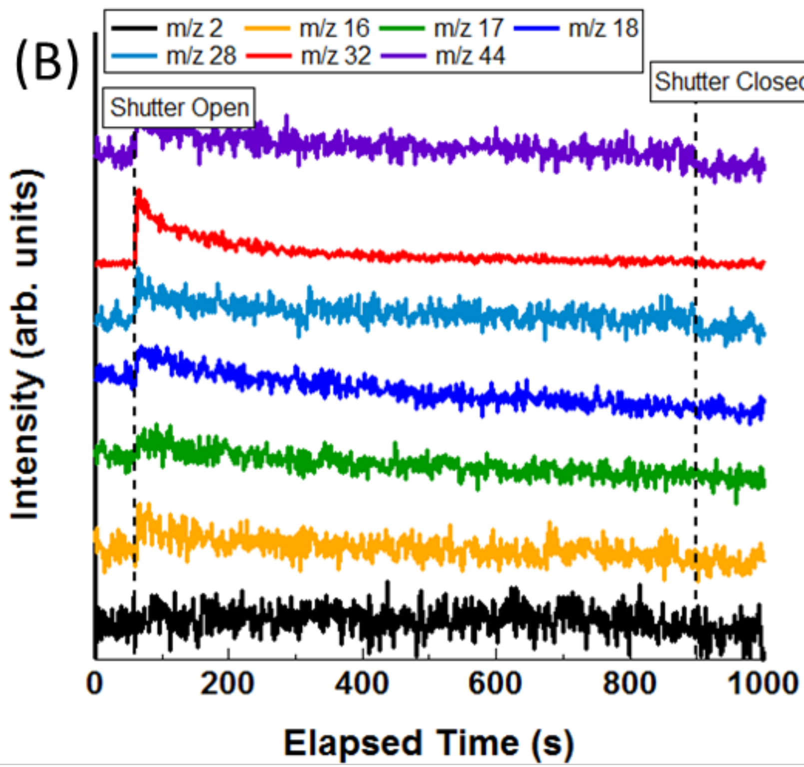
Patterned w/ 30 keV e$^-$
at 800 μC/cm^2



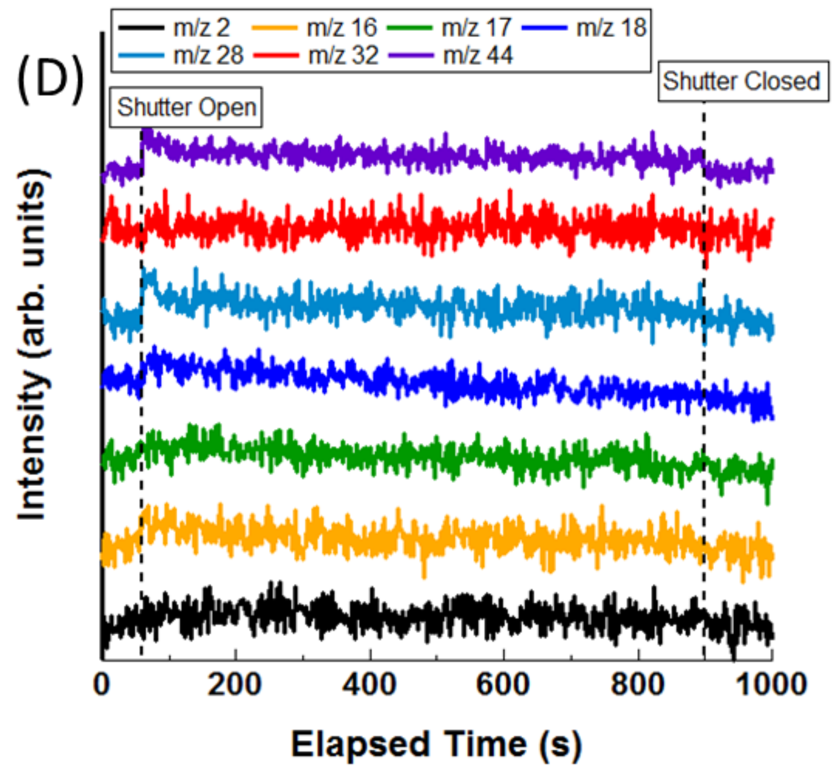
R. Oleksak, et al., ACS Appl. Mat. Interfaces 6, 2917 (2014)

Electron Stimulated Desorption HafSOx

HafSOx (w/ H_2O_2), E_{kin} = 80 eV

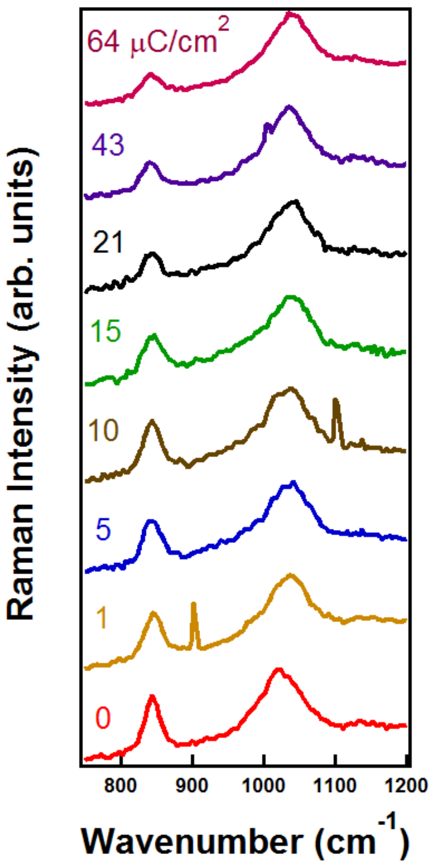


HafSOx (w/o H_2O_2), E_{kin} = 80 eV

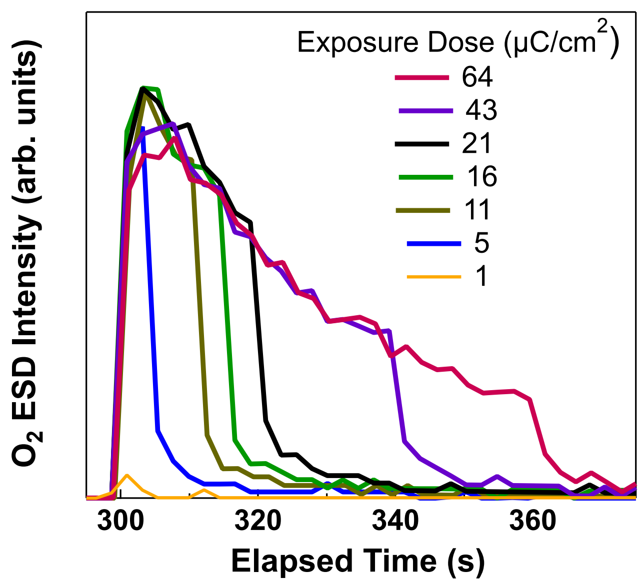


Significant O_2 desorption only from HafSOx films with peroxide.

Electron Stimulated Desorption HafSOx



HafSOx (w/ H_2O_2), E_{kin} = 500 eV

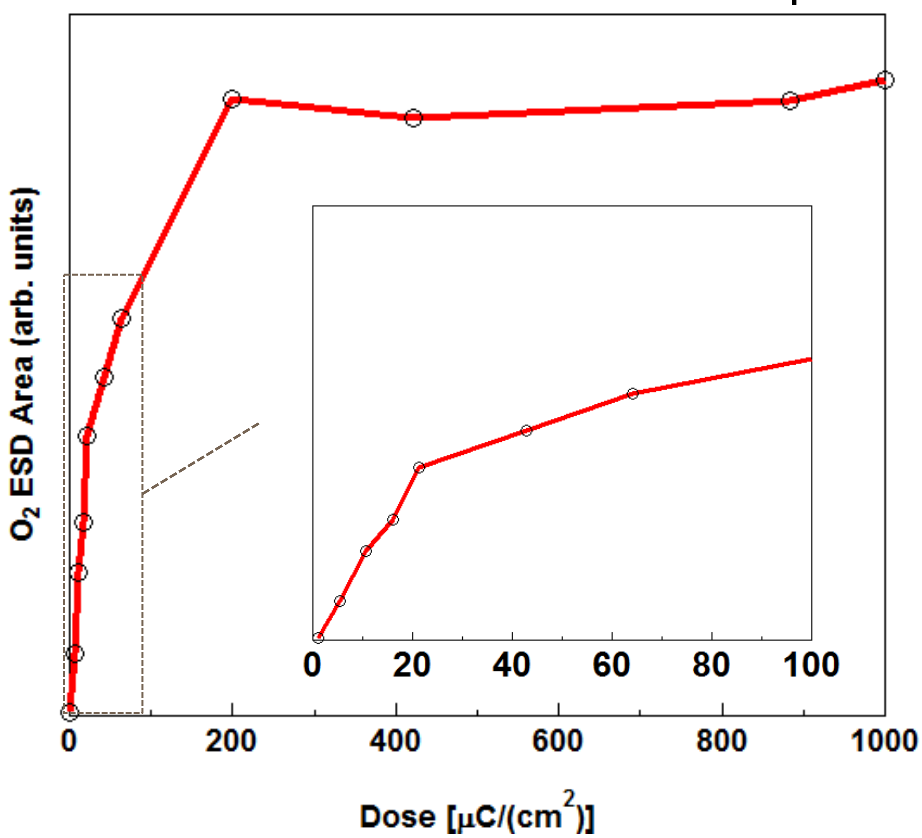


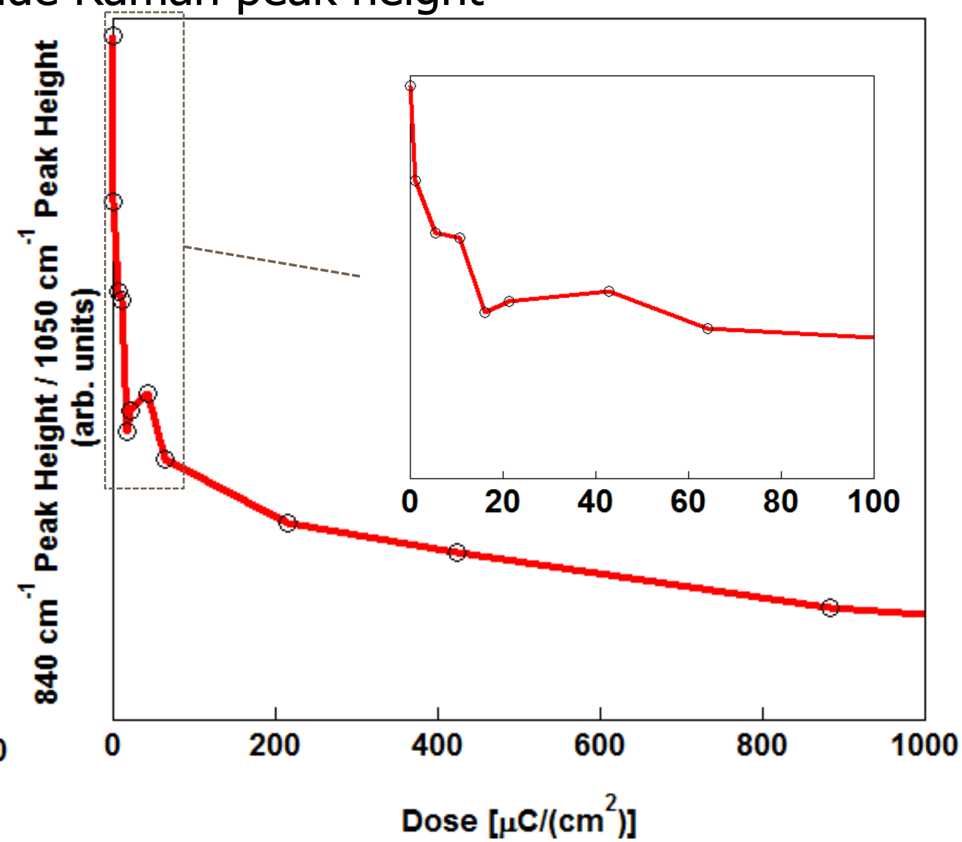
O_2 ESD curves for varying electron beam exposure times for 0.25M-Hf HafSOx films. Electron current = 1.07 μA/cm^2

- To understand initial electron induced chemistries in HafSOx
- O_2 desorption profiles were monitored for short exposure times
- Raman spectra for peroxide species (~840 cm^{-1}) were monitored as well
- Correlation found for increasing O_2 desorption and reduction in peroxide Raman signal

Comparison between Raman (bulk-sensitive) and ESD (surface-sensitive) techniques

Rapid increase in O_2 ESD area with corresponding decrease in peroxide Raman peak height

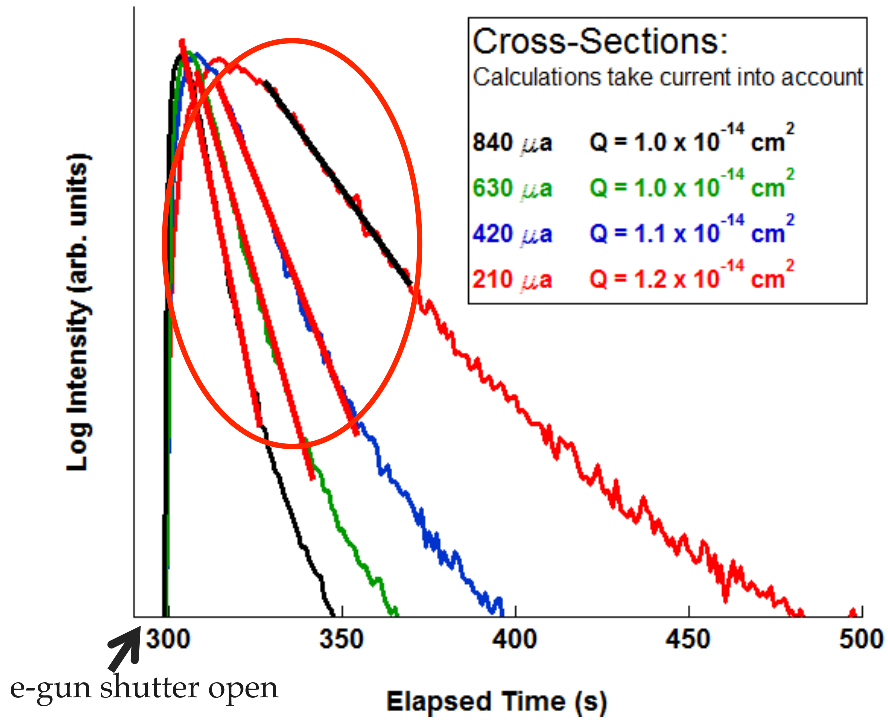




Relative peroxide height from Raman and area under O_2 ESD curves versus electron beam exposure times for 0.25M-Hf HafSOx films. Electron current = 1.07 μA/cm^2

Estimation of ESD Cross-Sections

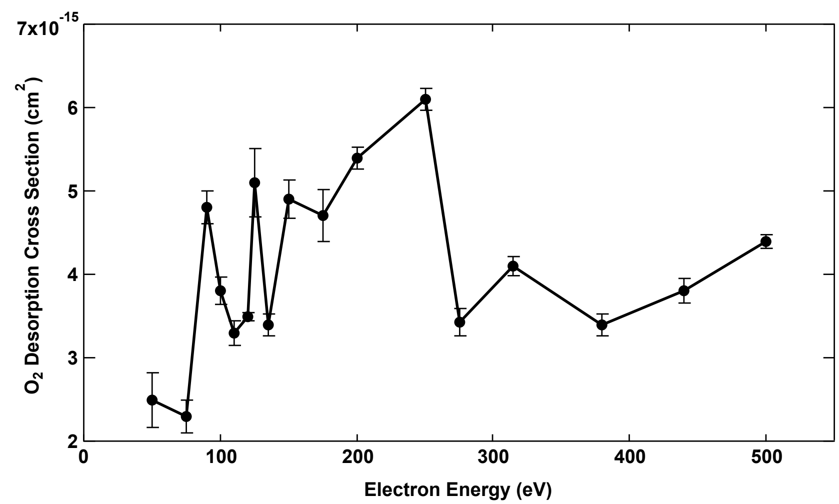
E_{kin} = 500eV



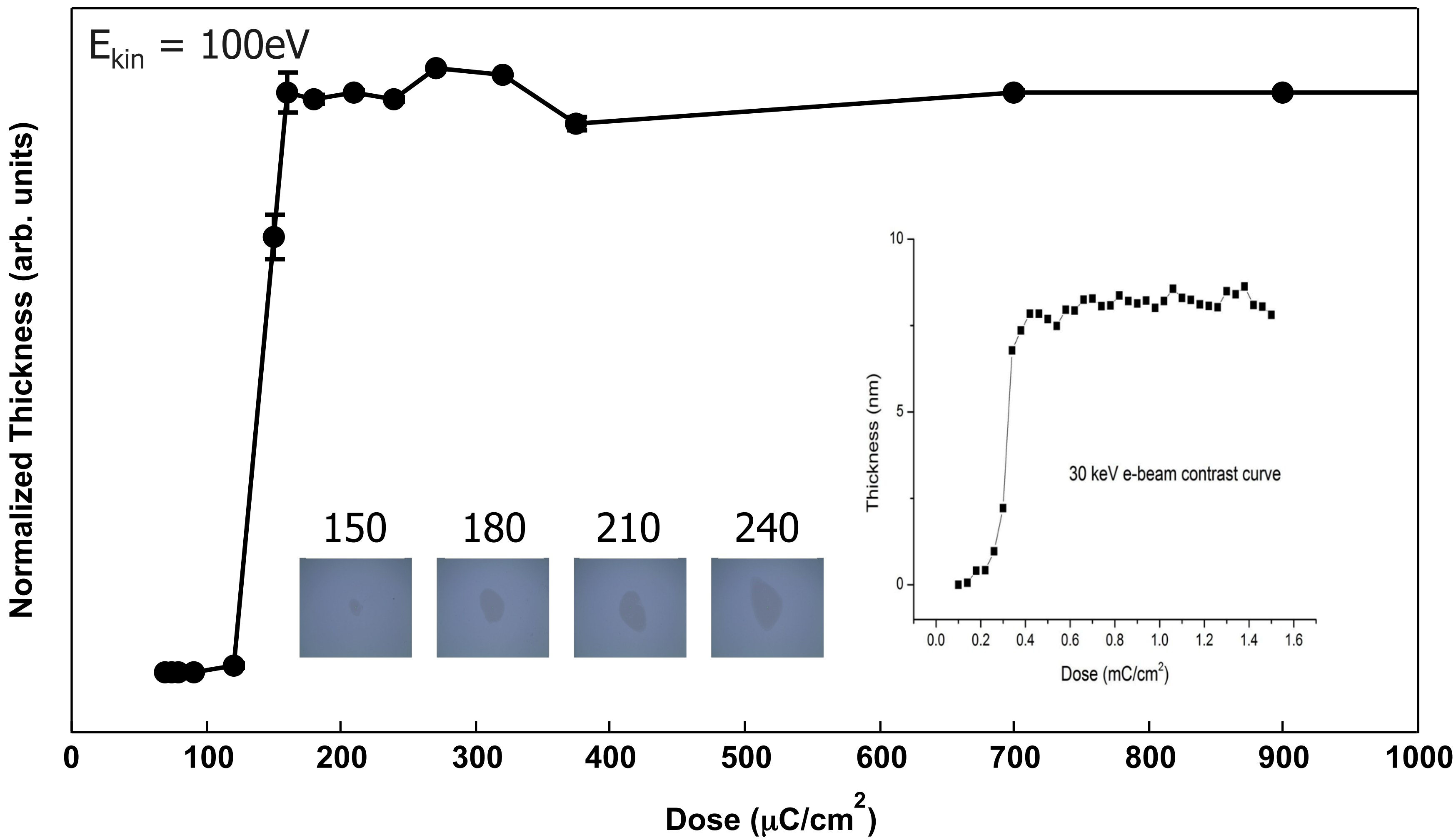
log O_2 desorption intensity for 0.15M-Hf HafSOx films for multiple current densities with 500eV beam energy.

$$QMS(t) \cong \beta \frac{J\sigma}{\epsilon} C_{O_2}(t)$$

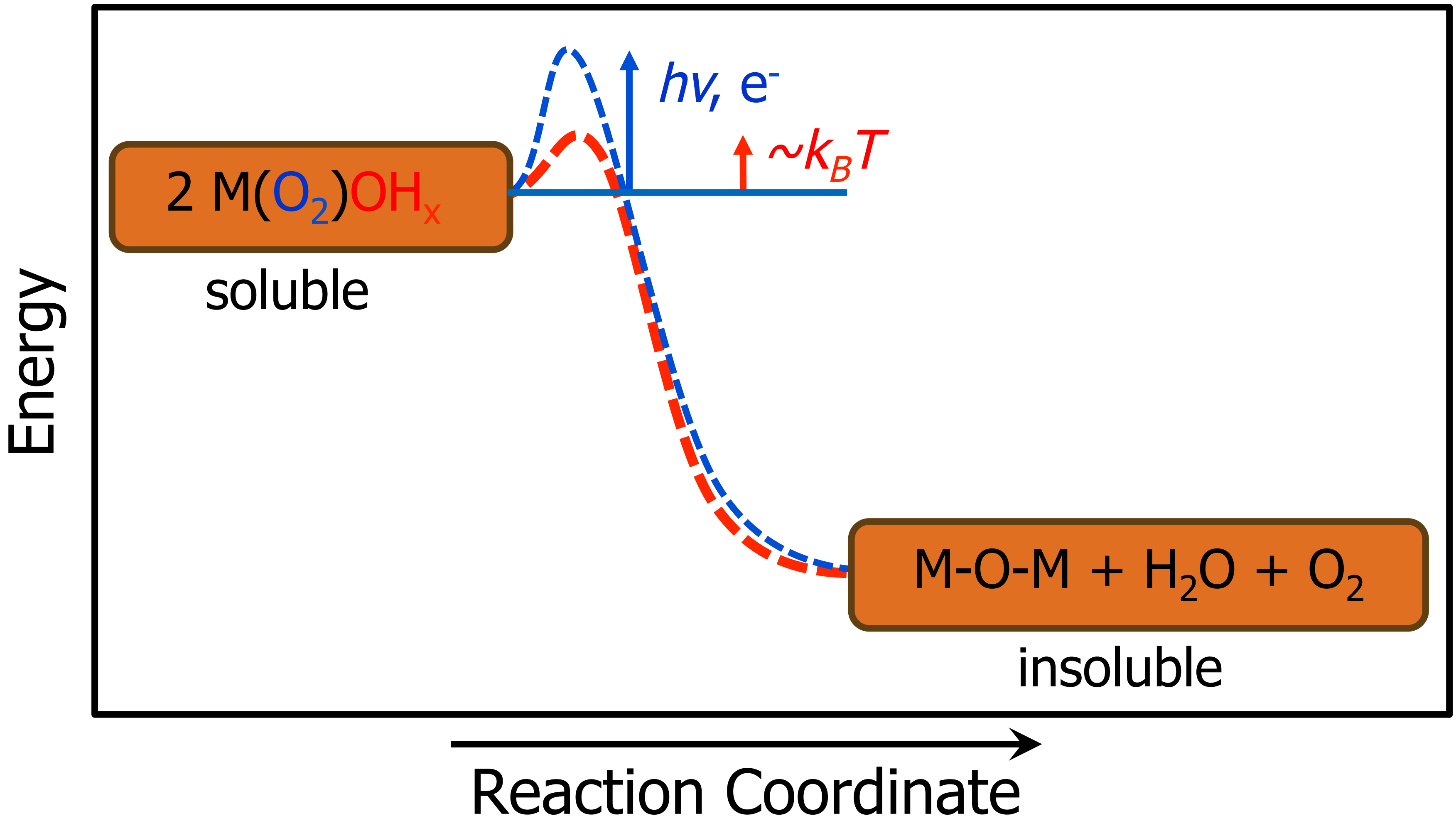
$$\frac{QMS(t)}{QMS_{init}} = exp\left\{\frac{JQ}{\epsilon} t\right\}$$



HafSOx Electron Contrast Curves



Competing Condensation Processes



Summary

- Nanodimensional patterning has been demonstrated using HafSOx.
- Addition of peroxo species to cluster provides radiation active species.
- Solubility transition dominated by thermal and/or radiation induced formation of Hf-O-Hf bonding in film.
- Electron stimulated desorption and temperature desorption indicates that H_2O and O_2 are main desorbing species.
- Methods being developed will be applied to other resist materials.

Acknowledgements

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center for sustainable materials chemistry

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